



US007067083B2

(12) **United States Patent**  
**Sekharipuram et al.**

(10) **Patent No.:** **US 7,067,083 B2**  
(45) **Date of Patent:** **Jun. 27, 2006**

(54) **HIGH REFRACTIVE INDEX  
THERMOPLASTIC POLYPHOSPHONATES**

(75) Inventors: **Venkat Sekharipuram**, Roanoke, VA (US); **Hosadurga K. Shobha**, Blacksburg, VA (US); **James E. McGrath**, Blacksburg, VA (US); **Atul Bhatnagar**, Roanoke, VA (US)

(73) Assignees: **Essilor International (Compagnie Generale D'Optique)** (FR); **Virginia Tech Intellectual Properties, Inc.**, Blacksburg, VA (US)

(\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 14 days.

(21) Appl. No.: **11/105,898**

(22) Filed: **Apr. 13, 2005**

(65) **Prior Publication Data**

US 2005/0179860 A1 Aug. 18, 2005

**Related U.S. Application Data**

(62) Division of application No. 10/642,922, filed on Aug. 18, 2003, now Pat. No. 6,943,221, which is a division of application No. 09/887,979, filed on Jun. 22, 2001, now Pat. No. 6,653,439, which is a division of application No. 09/439,825, filed on Nov. 12, 1999, now Pat. No. 6,288,210.

(51) **Int. Cl.**

**B29C 45/00** (2006.01)

**B29C 45/46** (2006.01)

**B29D 11/00** (2006.01)

**G02B 3/00** (2006.01)

**C08G 79/02** (2006.01)

(52) **U.S. Cl.** ..... **264/328.1**; 264/1.32; 525/588; 525/97; 525/210; 525/212; 528/398; 528/167; 528/176; 351/159

(58) **Field of Classification Search** ..... 264/328.1, 264/1.32; 525/588, 97, 210, 212; 528/398, 528/167, 176; 351/159

See application file for complete search history.

(56) **References Cited**

**U.S. PATENT DOCUMENTS**

3,719,727 A	3/1973	Masai et al.
3,946,093 A	3/1976	Koto et al.
4,039,512 A	8/1977	Kim et al.
4,093,582 A	6/1978	Mark et al.
4,206,296 A	6/1980	Yu et al.
5,679,804 A	10/1997	Ditrich et al.
6,040,416 A	3/2000	Sekharipuram et al.

**FOREIGN PATENT DOCUMENTS**

JP	51-114495	8/1976
SU	175651	10/1965

**OTHER PUBLICATIONS**

Concise Encyclopedia of Polymer Science and Engineering, p. 721, 1990.

Chemical Abstracts, 89 : 111437, Mark et al., 1978.

Chemical Abstracts, 86 : 17295, Okada et al., 1977.

Chemical Abstracts, 84 : 60204, Koto et al., 1976.

Chemical Abstracts, 122: 56712, Carraher et al., 1993.

Chemical Abstracts, 115 : 197854, Carraher et al., 1991.

Chemical Abstracts, 99 : 213370, Petreus et al., 1983.

Chemical Abstracts, 94 : 192931, Petreus et al., 1981.

*Primary Examiner*—Duc Truong

(74) *Attorney, Agent, or Firm*—Fish & Richardson P.C.

(57) **ABSTRACT**

High refractive index, melt processable polyphosphonates and methods for preparing the same are provided. These polymers are particularly useful for optical and ophthalmic parts, such as lenses. A method of preparing optical and ophthalmic lenses by injection molding the polymers of the present invention into the form of the optical or ophthalmic lenses is also provided.

**1 Claim, No Drawings**

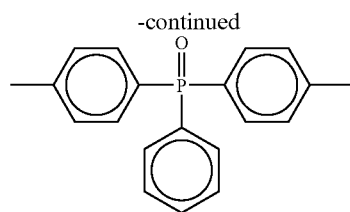
Chemical structures of benzene and biphenyl.

BrC1=CC=CC=C1C(C)C1=CC=CC=C1Br

The image displays three chemical structures, each with a line extending from it, indicating its role as a monomer in a polymerization reaction. The structures are:

- Top left:** 1,2-diphenylbenzene (o-biphenyl), consisting of two benzene rings connected at the 1 and 2 positions.
- Top right:** 1,2-bis(4-phenylphenyl)benzophenone, featuring a central benzophenone core (two benzene rings connected by a carbonyl group) with 4-phenylphenyl groups attached at the 1 and 2 positions.
- Bottom:** 1,2-bis(4-phenylphenyl)cyclohexane, consisting of a central cyclohexane ring with 4-phenylphenyl groups attached at the 1 and 2 positions.

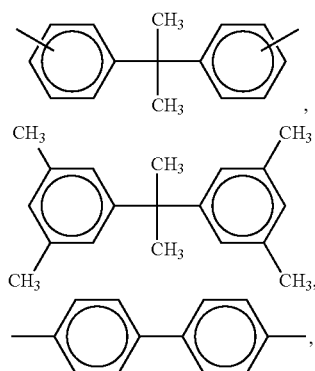
3



5

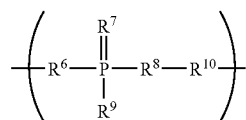
10

or any combination of any of the foregoing.  $R^1$  and  $R^3$  are preferably O. Preferably,  $R^2$  is S. Preferably,  $R^4$  is phenyl.  $R^5$  is preferably



or any combination of any of the foregoing.

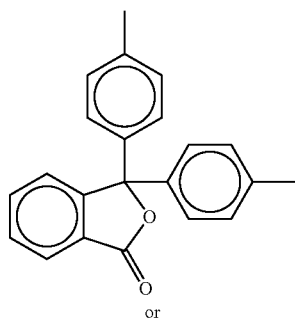
Another embodiment of the present invention encompasses melt-processable phosphonate homopolymers or copolymers comprising, consisting essentially of, or consisting of units of the formula:



40

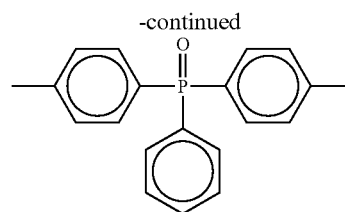
45

wherein  $R^6$ ,  $R^7$ , and  $R^8$  are independently O or S;  $R^9$  is a linear or branched  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  haloalkyl, phenyl, chlorophenyl, p-tolyl, benzyl, biphenyl, or cyclohexyl; and  $R^{10}$  is



or

4



5

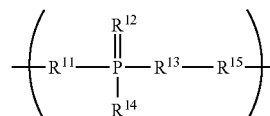
10

Preferably,  $R^6$  and  $R^8$  are O.

The invention further includes an optical or ophthalmic part, preferably a lens, comprising, consisting essentially of, or consisting of melt-processable phosphonate homopolymers or copolymers comprising units of the formula:

20

25



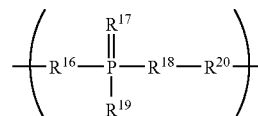
wherein  $R^{11}$ ,  $R^{12}$ , and  $R^{13}$  independently are O or S;  $R^{14}$  is a linear or branched  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  haloalkyl, phenyl, chlorophenyl, p-tolyl, benzyl, biphenyl, or cyclohexyl; and  $R^{15}$  is defined as  $R^5$  above. The optical or ophthalmic part may also be a transparent or translucent sheet comprising the melt-processable phosphonate polymers of formula III.

30

The polymers of the present invention can be homopolymers or copolymers, including, but not limited to, random copolymers and block copolymers. A preferred copolymer comprises a first unit having the formula

40

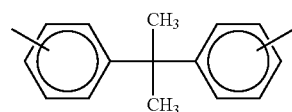
45



where  $R^{16}$ ,  $R^{17}$ , and  $R^{18}$  are independently O or S;  $R^{19}$  is phenyl; and  $R^{20}$  is

50

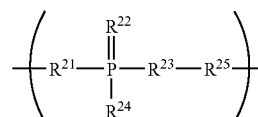
55



and a second unit having the formula

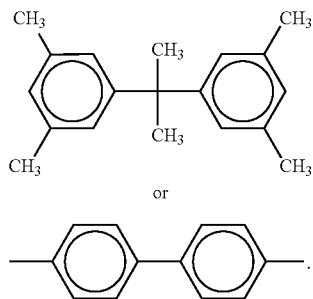
60

65



5

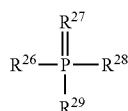
where  $R^{21}$ ,  $R^{22}$ , and  $R^{23}$  are independently O or S;  $R^{24}$  is phenyl; and  $R^{25}$  is



The number average molecular weight of a homopolymer or copolymer of the present invention is typically from about 10,000 to about 60,000 g/mol and preferably from about 15,000 to about 40,000 g/mol.

Generally, these homopolymers and copolymers have a glass transition temperature ( $T_g$ ) greater than or equal to about 120° C. Also, these polymers typically have a refractive index ranging from about 1.58 to about 1.64. These polymers are typically processable at from about 75 to about 100° C. above their glass transition temperatures.

The melt-processable phosphonate homopolymers and copolymers of the present invention may be prepared as described in Japanese Patent Publication No. 61-261321. One method of preparing these polymers is as follows. At least one phosphonic acid halide having the formula



Formula IV

where  $R^{26}$  and  $R^{28}$  are independently halogens;  $R^{27}$  is O or S; and  $R^{29}$  is a linear or branched  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  haloalkyl, phenyl, chlorophenyl, p-tolyl, benzyl, biphenyl, or cyclohexyl is reacted with one or more bisphenols to yield the phosphonate homopolymer or copolymer. Preferred phosphonic acid halides include phenyl phosphonic dichloride, phenyl thiophosphonic dichloride, and any combination of any of the foregoing. The phosphonic acid halide may be dissolved by mixing it in a solvent, such as methylene chloride, prior to reacting the phosphonic acid halide with the bisphenol. When preparing polymers having units of the formula I or II above,  $R^{27}$  and  $R^{29}$  of the phosphonic acid halide are defined as  $R^2$  and  $R^4$  or  $R^7$  and  $R^9$  above, respectively.

Suitable bisphenols include, but are not limited to, hydroquinone; resorcinol; 4,4'-dihydroxybiphenyl; 4,4'-cyclohexyldenediphenol; bisphenol A; bis(4-hydroxyphenyl) methane; 2,2-bis(2-hydroxyphenyl)propane; bis P; 4,4'-bis-S; 2,2'-bis-S; 2-hydroxyphenyl-4'-hydroxyphenyl sulfone; dihydroxydiphenyl ether; bis(4-hydroxyphenyl) sulfide; bis(2-hydroxyphenyl) sulfide; dihydroxybenzophenone; 1,5-dihydroxynaphthalene; 2,5-dihydroxynaphthalene; 2,2-bis(3,5-dimethyl-4-hydroxyphenyl) propane; thiodithiophenol; phenolphthalein; 4,4'-bis(hydroxyphenyl)phenyl phosphine oxide;  $\alpha,\alpha'$ -bis(4-hydroxy-3-methylphenyl)-1,4-diisopropylbenzene; bis E; 2,2-bis(4-hydroxy-3-methylphenyl) propane; bis(4-hydroxy-3-methylphenyl) sulfide; dihydroxydiphenylether; 1,3-bis(4-hydroxyphenoxy) benzene; phenyl

6

HC; t-butyl HQ; 4,4'-thiobis(t-butyl cresol); 2,2'-thiobis(4-t-octylphenol); and any combination of any of the foregoing. The bisphenol may be dissolved by mixing it in a solvent, such as methylene chloride with triethylamine and 1-methyl imidazole, prior to reacting the bisphenol with the phosphonic acid halide.

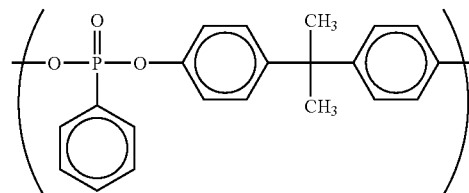
The copolymer of the present invention may be prepared by reacting at least two different phosphonic acid halides having the aforementioned formula with one or more bisphenols. Alternatively, the copolymer may be prepared by reacting at least one phosphonic acid halide with at least two different bisphenols.

Optical or ophthalmic lenses may be prepared by injection or compression molding a melt-processable phosphonate polymer of the present invention into the form of a lens.

The following examples illustrate the invention without limitation.

## EXAMPLE 1

A 4-necked, 500 mL round bottomed flask equipped with an overhead stirrer, nitrogen inlet, temperature probe, dropping funnel and a condenser, was flame dried three times and cooled to room temperature each time under a strong purge of dry nitrogen. 20.546 g (0.09 moles) of bisphenol A, 120 mL of dry distilled methylene chloride, 27.5 mL (0.198 moles) of dry distilled triethylamine (10% excess), and 0.24 mL (0.003 moles) of 1-methyl imidazole was added to the flask. The mixture was stirred until the bisphenol A was completely dissolved. The flask was cooled to about 0° C. with stirring. A solution of 17.549 g (0.09 moles) of distilled phenylphosphonic acid dichloride in 60 mL of dry methylene chloride was added dropwise from a dropping funnel over about 40–60 minutes while the flask was maintained at about 0° C. and the mixture was stirred. After completion of the dropwise addition, stirring was continued for another hour. A solution of 1.367 g (0.00091 moles) t-butylphenol in 15 mL of methylene chloride was added to the mixture and the mixture was stirred for 30 minutes. The mixture was washed with 0.5 N aqueous hydrochloric acid and then repeatedly washed with water until the aqueous phase was neutral. The mixture was poured into rapidly stirred methanol and allowed to coagulate. The polymer was dried and dissolved in about 15–20% w/v tetrahydrofuran (THF) and allowed to coagulate in the water to form a free flowing fibrous polymer. The polymer was dried in a vacuum oven at about 90–95° C. This polymer comprised units having the formula



## EXAMPLES 2–5

The procedure in Example 1 was repeated except bis P, 4,4'-biphenol, 4,4'-cyclohexyldenediphenol, or phenolphthalein was substituted for bisphenol A in Examples 2–5, respectively. The polymers prepared comprised units having the formulas in Table 1 below.

TABLE 1

Example	Units
2	
3	
4	
5	

## EXAMPLE 6

Tough, ductile films and plaques were formed from the polymers prepared in Examples 1–5 by compression molding and their refractive index, number average molecular weight ( $M_n$ ), and glass transition temperature ( $T_g$ ) were determined. The results are shown in Table 2 below.

TABLE 2

Example	Refractive Index Value	$M_n$	$T_g$ (° C.)
1	1.60	44,000	117
2	1.60	33,000	124
3	1.639	21,500	145
4	1.606	19,100	130
5	1.623	26,000	186

The tensile properties of the polymer prepared in Example 1 were determined and are shown in Table 3 below.

45

TABLE 3

Modulus (GPa)	Yield Stress (MPa)	Yield Strain (%)	Stress at Break (MPa)	Strain at Break (%)
1.30 ± 0.1	67.5 ± 3.2	9.3 ± 0.5	45.5 ± 3.4	54.2 ± 20.0

50

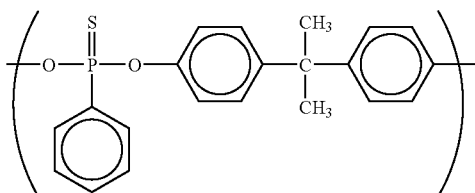
## EXAMPLE 7

A first solution of phenyl thiophosphonic dichloride in methylene chloride was added dropwise over about 1 hour to a second solution of bisphenol A, triethylamine, and N-methyl imidazole, while the second solution was maintained at about 0° C. and stirred. After completion of the dropwise addition, the solution was warmed to room temperature and stirred for about 10 hours. The mixture was then washed with water. The mixture was poured into rapidly stirred methanol and allowed to coagulate to form a polymer. The polymer was dried and dissolved in about 15–20% w/v tetrahydrofuran (THF) and allowed to coagulate in the water to form a free flowing fibrous polymer. The polymer was dried in a vacuum oven at about 90–95° C. This polymer comprised units having the formula

55

60

65



The refractive index, number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), and polydispersity index ( $P_d$ ) of the polymer were determined. The results are shown in Table 4 below.

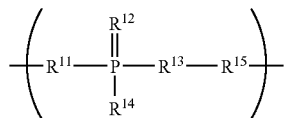
TABLE 4

Refractive Index	M <sub>n</sub>	M <sub>w</sub>	P <sub>d</sub>
1.629	29,000	59,000	2.01

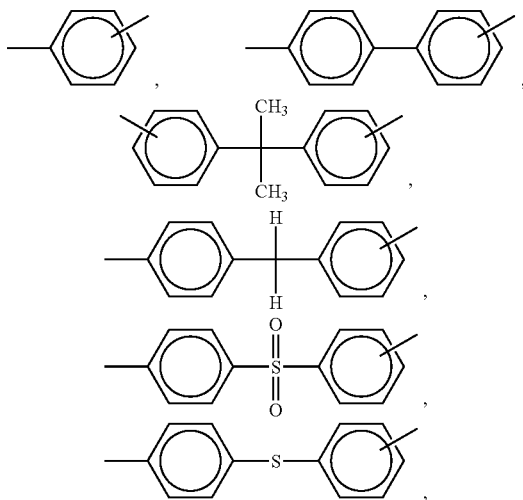
All patents, publications, applications, and test methods mentioned above are hereby incorporated by reference. Many variations of the present matter will suggest themselves to those skilled in the art in light of the above detailed description. All such obvious variations are within the patented scope of the appended claims.

What is claimed is:

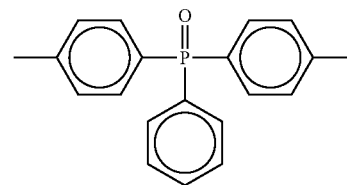
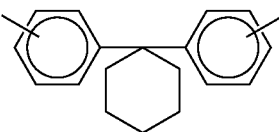
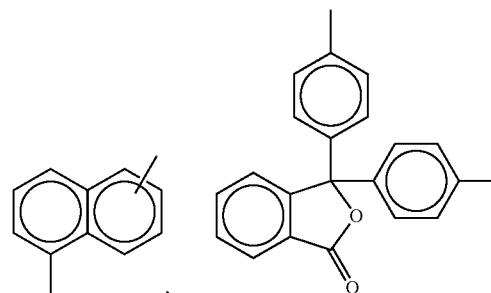
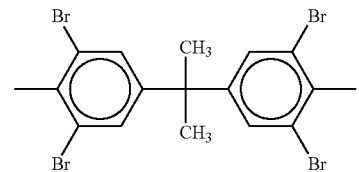
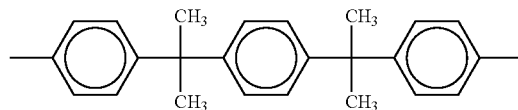
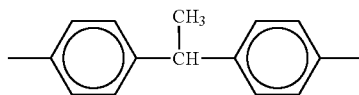
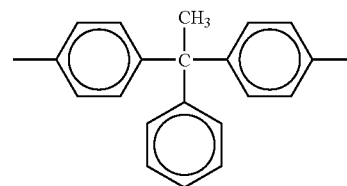
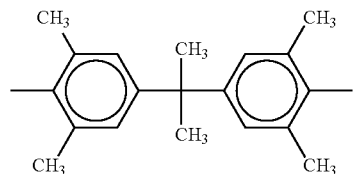
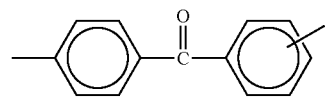
1. A method for preparing an optical or ophthalmic lens, said method comprising injection molding into the form of said lens, a melt-processable phosphonate homopolymer or copolymer having units of the formula:



wherein  $R^{11}$ ,  $R^{12}$ , and  $R^{13}$  independently are O or S;  $R^{14}$  is a linear or branched  $C_1$ – $C_4$  alkyl or  $C_1$ – $C_4$  haloalkyl, phenyl, chlorophenyl, p-tolyl, benzyl, biphenyl, or cyclohexyl; and  $R^{15}$  is



-continued



\* \* \* \* \*